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## **Description**

# PROCESS FOR FORMING A PHOSPHATE CONVERSION COATING ON METAL

# FIELD AND BACKGROUND OF THE INVENTION

This invention relates to processes for the phosphate conversion treatment of metals wherein said processes employ a nickel ion-free phosphate conversion treatment bath and produce a uniform, strongly paint-adherent, and highly post-painting corrosion-resistant coating on such metals as steel sheet, zinc-plated steel sheet, aluminum alloys, and magnesium alloys.

Phosphate conversion treatments are currently executed as a pre-paint treatment on automotive body components in order to enhance corrosion resistance and improve the steel sheet-to-paint adherence. In these phosphate conversion treatments, the metal is first brought into contact with a colloidal titanium surface conditioning bath and is then brought into contact with an acidic solution containing phosphate ions, zinc ions, nickel ions, and manganese ions in order to precipitate a phosphate coating on the metal.

However, in association with today's heightened concern with environmental protection, the regulatory situation with regard to nickel in wastewater has become increasingly stringent, particularly in Europe. It is certainly prudent to anticipate that regulations on nickel in wastewater might also become much more demanding in other countries in the future. These considerations make it desirable to eliminate the nickel from the conversion treatment baths used in zinc phosphate treatments.

Unfortunately, a number of negative effects are caused by removal of the nickel from many phosphate treatment baths used in the aforementioned phosphate treatment processes: The crystals in the phosphate coating undergo coarsening; the phosphate coating suffers from a loss of uniformity, the post-painting corrosion resistance declines, and the secondary (water-resistant) adherence of paint to zinc-plated material also declines.

Japanese Laid Open Patent Application (PCT) Number Hei 7-505445 (505,445/1995) teaches a nickel-free phosphate treatment process in order to solve the problems referenced above. This treatment process involves formation of a nickel-free phosphate coating by treatment with a phosphate conversion bath containing 0.2 to 2 grams of zinc ions per liter of bath (this unit of concentration being freely used hereinafter for any constituent of any liquid and being usually abbreviated as "g/l"), 0.5 to 25 milligrams of copper ions per liter, and 5 to 30 g/l phosphate ions. This process

uses copper as a substitute metal for nickel, but still suffers from several problems. Since the allowable copper level in this conversion treatment bath is so very low, management of the copper concentration in real-world lines is exceedingly difficult. Another concern is with electrolytic corrosion of the equipment accompanied by displacement copper plating on parts of the equipment.

Given this background, there is a desire for development of a phosphate conversion treatment process that does not use nickel but nevertheless affords a post-painting adherence and post-painting corrosion resistance that are the equal of those afforded by existing phosphate conversion treatments that use nickel. One major object of this invention is to provide a phosphate conversion treatment process that treats metal surfaces with a nickel-free conversion treatment bath and produces a phosphate conversion coating that evidences an excellent post-painting corrosion resistance and excellent paint adherence.

#### BRIEF SUMMARY OF THE INVENTION

It has been found that most or all of the problems caused by the removal of nickel from previous phosphating treatments can be eliminated by using a surface conditioning composition that contains very fine, dispersed solid phosphate particles.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

More specifically, a process according to the invention for forming a phosphate conversion on a metal substrate surface comprises, preferably consists essentially of, or more preferably consists of the following operations:

- (I) contacting the metal substrate surface with an aqueous liquid surface conditioning composition (hereinafter for brevity often called a "bath" without intending any implication that it must be contacted with the metal substrate by immersion of the metal substrate in a volume of the aqueous liquid surface conditioning composition) that comprises, preferably consists essentially of, or more preferably consists of, water and the following components:
- (I.A) dispersed solid phosphate particles that:
  - have a diameter no greater than 5 micrometres, this unit of length being hereinafter usually abbreviated as "μm"; and
  - (ii) comprise, preferably consist essentially of, or more preferably consist of, at least one substance selected from the group consisting of phosphates that contain at least one divalent or trivalent metal cation; and
- (I.B) as adhesion-promoting component, at least one selection from the group

consisting of the following subgroups:

- (1) monosaccharides, polysaccharides, and derivatives thereof;
- (2) phosphorus containing solutes selected from the group consisting of orthophosphoric acid, condensed phosphoric acids, and organophosphonic acid compounds;
- (3) water-soluble polymers that are homopolymers or copolymers of vinyl acetate and derivatives of these homopolymers and copolymers; and
- (4) copolymers and polymers as afforded by the polymerization of:
  - (a) at least one selection from:
    - -- monomers, exclusive of vinyl acetate, that conform to general chemical formula (I):

$$R^{1}$$
  
 $H_{2}C=C-COOR^{2}$  (I),  
where  $R^{1}=H$  or  $CH_{3}$  and  $R^{2}=H$ ,  $C_{1}$  to  $C_{5}$  alkyl, or  $C_{1}$  to  $C_{5}$  hydroxyalkyl; and

- other  $\alpha,\beta$ -unsaturated carboxylic acid monomers; and, optionally,
- (b) not more than 50 % by weight of monomers that are not vinyl acetate and are not within the description of part (a) immediately above but are copolymerizable with said monomers that are within the description of said part (a);

and

- (II) contacting the metal substrate surface as conditioned in operation (I) as described above with a nickel-free phosphate conversion treatment bath that comprises, preferably consists essentially of, or more preferably consists of water and the following amounts of the following components:
- (II.A) from 0.5 to 5 g/l of zinc cations;
- (II.B) from 5 to 30 g/l of phosphate ions; and
- (II.C) a component of conversion accelerator.

In a preferred embodiment, the above-specified conversion treatment baths also contain from 0.1 to 3.0 g/l of at least one type of metal containing ions selected from the group consisting of magnesium ions, cobalt ions, manganese ions, calcium ions, tungstate ions, and strontium ions.

The features of this invention are explained in greater detail hereinbelow.

Whenever a group of materials from which a constituent can be selected is specified, whether by a specific list, use of generic chemical terms, and/or conformance to a general chemical formula, any two or more of the group may be selected instead of a single member with equal preference, unless explicitly stated otherwise.

While no particular limitations apply to the metal on which the inventive phosphate treatment process may be executed, this metal is preferably steel sheet, zinc-plated steel sheet, zinc alloy-plated steel sheet, magnesium alloy, or aluminum alloy.

It is preferred in the practice of the invention that the metal substrate surface be clean prior to the phosphate conversion treatment. Metal whose surface is already clean can be brought without further treatment into contact with the surface conditioning bath. However, in the case of treatment of metal whose surface is contaminated with adherent materials such as iron particles, dust, and oil, the contaminants adhering on the surface should be removed by cleaning, for example, by cleaning with a water-based alkaline degreaser or an emulsion degreaser or by solvent degreasing. When a water-based cleaner is used, the cleaning bath remaining on the metal surface is preferably removed by the provision of, for example, a water rinse step after the cleaning step.

At least some of the particles of divalent and/or trivalent metal phosphate present in a surface conditioning bath in a process according to the invention must have a particle size or diameter no greater than 5  $\mu m$ . (Insolubles of larger size are undesirable because — depending on the particular circumstances — they often cannot be stably maintained in the aqueous bath.) These phosphate particles are believed to function as nuclei during phosphate crystal deposition and also to promote the deposition reaction itself, by undergoing partial dissolution in the phosphate conversion treatment bath and inducing a substantial acceleration of the initial phosphate crystal deposition reactions by supplying one or more main components of the phosphate crystals to the region immediately adjacent to the metal surface.

The divalent and trivalent metals used here are not critical, but preferably comprise at least one selection from Zn, Fe, Mn, Co, Ca, Mg, and Al. The divalent and/or trivalent metal phosphate particles are preferably present at a concentration from 0.001 to 30 g/l. Acceleration of the initial phosphate crystal deposition reactions does not normally occur at a divalent and/or trivalent metal phosphate particle concentration below 0.001 g/l due to the small amount of divalent and/or trivalent metal phosphate

particles that become adsorbed on the metal surface at such low concentrations. Concentrations below 0.001 g/l also prevent acceleration of the crystal deposition reactions due to the small number of divalent and/or trivalent metal phosphate particles available to act as crystal nuclei. Divalent and/or trivalent metal phosphate particle concentrations in excess of 30 g/l cannot be expected to provide additional promotion of the phosphate conversion reactions and hence will be uneconomical.

The adhesion-promoting component that must be present in the inventive surface conditioning bath functions to improve the dispersion stability of the divalent and/or trivalent metal phosphate particles and to accelerate adsorption of the divalent and/or trivalent metal phosphate particles onto the metal surface. More specifically, the adhesion promoting component is believed to adsorb on the surface of the divalent and/or trivalent metal phosphate particles and, through a steric hindrance activity and repulsive forces arising from its electrical charge, to prevent collisions among the divalent and/or trivalent metal phosphate particles in the surface conditioning bath and thereby inhibit their aggregation and sedimentation. In addition, due to its structure, the adhesion-promoting component itself is believed to have an ability to adsorb to metal surfaces and thereby to accelerate adsorption to metal surfaces by the divalent and/or trivalent metal phosphate particles, so that the surface conditioning activity manifests upon contact between the metal workpiece and surface conditioning bath.

The adhesion-promoting component concentration is preferably from 1 to 2,000 parts by weight of the adhesion promoting component per 1000 parts by weight of the total conditioning composition, this unit of concentration being hereinafter usually abbreviated as "ppm". At concentrations below 1 ppm a surface conditioning activity can not usually be produced just by contact between the metal workpiece and the surface conditioning bath. Not only can no additional benefit be expected at concentrations in excess of 2,000 ppm, but such concentrations can impair the phosphate conversion coating formed, perhaps as a result of excessive adsorption of the adhesion promoting component on the metal substrate surface.

A saccharide type of adhesion-promoting component for the surface conditioning operation in a process according to the invention may be exemplified by fructose, tagatose, psicose, sorbose, erythrose, threose, ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, and the sodium and ammonium salts of all of these saccharides.

A phosphorus containing acid type of adhesion-promoting component in the sur-

face conditioning process is exemplified by orthophosphoric acid, polyphosphoric acids, and organophosphonic acid compounds, or more individually by pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid, hexametaphosphoric acid, aminotrimethylenephosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetramethylenephosphonic acid, diethylenetriamine-pentamethylenephosphonic acid, and the sodium and ammonium salts of all of the preceding acids. Sodium salts are preferred for the organophosphonic acids if they are to be used in salt form.

Polymeric adhesion promoting components derived from polyvinylacetate in a surface conditioning operation in a process according to the invention are exemplified by polyvinyl alcohols afforded by the hydrolysis of vinyl acetate polymers, cyanoethylated polyvinyl alcohols afforded by the cyanoethylation of polyvinyl alcohol with acrylonitrile, formalated polyvinyl alcohols afforded by the acetalation of polyvinyl alcohol with formaldehyde, urethanized polyvinyl alcohols afforded by the urethanation of polyvinyl alcohol with urea, and water-soluble polymers afforded by the introduction of carboxyl moieties, sulfonic moieties, or amide moieties into polyvinyl alcohol. Suitable vinyl acetate-copolymerizable monomers are exemplified by acrylic acid, crotonic acid, and maleic anhydride. The effects associated with the present invention will be fully manifested as long as the vinyl acetate polymer or derivative thereof or the copolymer of vinyl acetate and vinyl acetate-copolymerizable monomer is soluble in water. Within this limitation, these effects are independent of the degree of polymerization and the degree of functional group introduction of the subject polymers.

Suitable monomers for other polymeric adhesion promoting components for the surface conditioning operation are exemplified by: methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hydroxymethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypentyl acrylate, hydroxymethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, and hydroxypentyl methacrylate as examples of polymers according to formula (I); acrylic acid, methacrylic acid, and maleic acid as unsaturated acids; and styrene, vinyl chloride, and vinylsulfonic acid as optional comonomers.

A surface conditioning bath used by the inventive phosphate treatment processes can also optionally contain an alkali metal salt or ammonium salt or a mixture thereof, selected from the group consisting of orthophosphate salts, metaphosphate salts, orthosilicate salts, metasilicate salts, carbonate salts, bicarbonate salts, nitrate

salts, nitrite salts, sulfate salts, borate salts, organic acid salts, and combinations of two or more selections from the aforesaid alkali metal and ammonium salts. The concentration of this component is not critical, but when used is preferably from 0.5 to 20 g/l. The surface conditioning bath may also contain a surfactant to promote uniform wetting of the surface being treated.

The phosphate conversion treatment process of this invention will now be considered in greater detail. A zinc ions concentration below 0.5 g/l, because it can prevent the formation of a coating of acceptable weight and can result in a diminished coverage ratio by the deposited phosphate crystals, can produce an inadequate post-painting corrosion resistance. A zinc ions concentration in excess of 5.0 g/l can cause a coarsening of the coating crystals, resulting in particular in a decline in the post-painting adherence. The use of a phosphate ions concentration below 5.0 g/l strongly impairs the production of a normal conversion coating. Concentrations in excess of 30.0 g/l are uneconomical since they provide no additional effect. Phosphate ions can be supplied by the addition of phosphoric acid or its aqueous solution to the phosphate conversion treatment bath or by the dissolution of, for example, sodium, magnesium, or zinc phosphate in the phosphate conversion treatment bath.

The conversion treatment bath also contains a component known as a "conversion accelerator" or simply "accelerator". The accelerator acts to restrain gaseous hydrogen production during etching, an action sometimes called "depolarizing" the metal substrate surface. Otherwise, however, no particular limitations apply to the accelerator, and any material or combination of materials recognized as a conversion accelerator in prior art may be used.

The phosphate conversion treatment bath of this invention can also contain from 0.1 to 3.0 g/l of at least one type of metal containing ions selected from the group consisting of magnesium cations, cobalt cations, manganese cations, calcium cations, tungstate anions, and strontium cations. The presence of this component in the phosphate conversion treatment bath, through its incorporation into the phosphate coating and through its precipitation in a form separate from the phosphate, provides additional performance enhancements in the post-painting corrosion resistance and post-painting adherence, respectively. The use of a concentration below 0.1 g/l usually does not effect any improvement in painting performance. A concentration above 3.0 g/l is economically wasteful, since no additional improvements in painting performance usually results; a high concentration can actually hinder deposition of the zinc phosphate that

is the main component of an effectively protective conversion coating produced according to this invention. The source of one of the types of metal cations can be, for example, an oxide, hydroxide, carbonate, sulfate, nitrate, or phosphate of the particular metal. The source of tungstate can be, for example, the sodium or potassium salt.

An etchant may be added to the phosphate conversion treatment bath in order to induce a uniform etch of the surface of the metal workpiece. Usable as this etchant are, for example, fluoride ions and complex fluoride ions such as fluorosilicate ions. The fluorine compound used here can be, for example, hydrofluoric acid, fluorosilicic acid, or a water soluble metal salt (e.g., sodium salt, potassium salt) of the preceding.

The phosphate conversion treatment can be carried out by immersion or spraying or some combination thereof. Treatment for about 1 to 5 minutes can form a conversion coating satisfactorily robust for practical applications. The temperature of the phosphate conversion treatment bath is preferably from 30 to 60 °C.

The phosphate conversion treatment is preferably followed by at least one water rinse, and deionized water is preferably used in the final water rinse.

Working and comparative examples of actual treatments are provided below in order to demonstrate the advantageous effects of this invention in specific terms. The working examples that follow are simply examples of the application of the invention and in no way limit the applications of the invention or materials usable in the application of the invention.

## **Materials tested**

The following metal substrates were treated in the working and comparative examples: electrogalvanized steel sheet ("EG"), sheet thickness = 0.8 millimeters (hereinafter usually abbreviated as "mm"), plating add-on = 20 grams of plated zinc per square meter of sheet surface, this unit of coating weight being hereinafter freely used for any coating on any surface and being hereinafter usually abbreviated as "g/m²; galvannealed hot-dip galvanized steel sheet ("GA"), sheet thickness = 0.8 mm, coating add-on =  $45 \text{ g/m}^2$ ; and cold-rolled steel sheet ("CRS"), sheet thickness = 0.8 mm, type SPCC-SD.

**Treatment operations sequence** (common to the working and comparative examples; as noted in the description of the testing below, not all of the specimens tested were subjected to the operations numbered 8 or higher)

(1) Degreasing with diluted FINECLEANER® L4460 alkaline degreaser concentrate, a product of Nihon Parkerizing Co., Ltd., the working degreaser containing 20

g/l of agent A and 12 g/l of agent B, 43 °C, 120 seconds, dipping.

- (2) Water rinse with tapwater: ambient temperature, 30 seconds, spray.
- (3) Surface conditioning

The conditions are described below in the tables for the working and comparative examples. The colloidal titanium surface conditioning treatments were run using PREPALENE® ZN, a product of Nihon Parkerizing Co., Ltd.

- (4) Phosphate conversion treatment The conditions are described below in the tables for the working and comparative examples. The treatment time was 120 seconds in all cases.
- (5) Water rinse (tapwater): ambient temperature, 30 seconds, spray
- (6) Deionized water rinse (deionized water with an electrical conductivity ≤ 0.2 microSiemens per centimeter): ambient temperature, 20 seconds, spray
- (7) Drain/dry: 120 seconds, forced hot air at 90 °C
- (8) Cationic electrocoating to a film thickness of about 20  $\mu$ m, then bake for 20 minutes at 180 °C
- (9) Surface coating with a film thickness of about 40 μm baked for 20 minutes at 140°C
- (10) Top coating with a film thickness of about 40 μm baked for 20 minutes at 140 °C.

#### Test and other evaluation methods

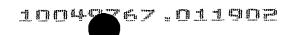
The coating appearance was evaluated on the following two-level scale (after operation (7) as described above:

- + : the coating was uniform;
- the coating exhibited a significant lack of uniformity with visible voids.

The test conditions and evaluation scale for the secondary (water-resistant) adherence were as follows: The sheet after operation (10) as described above was immersed for 240 hours in a hot water bath (maintained at 40 °C) that was being bubbled with air. The sheet was allowed to stand for 2 hours after removal from the hot water bath, after which time the peeling behavior was evaluated by cutting a grid (2 mm on each edge) in the sheet and subjecting this to tape peeling. The peeling behavior was evaluated using the following three-level scale:

- ++ : complete absence of peeling;
- some peeling observed at the edges of the grid cut;
- substantial peeling.

The test conditions and evaluation scale for the hot saltwater immersion test



were as follows. A cross cut was scribed with an acrylic cutter in the sheet after operation (8) as described above, and the specimen thus prepared was immersed for 240 hours in a 5 % by weight solution of sodium chloride in water that was maintained at 55 °C and was bubbled with air. The specimen was allowed to stand for 1 hour after withdrawal from the saltwater bath, after which time the cross cut was peeled with tape and the width of peeling from the cut was evaluated. The peeling behavior was evaluated using the following three-level scale:

#### For the CRS:

+ + : maximum peel width (both sides) less than 4 mm;

+ : maximum peel width (both sides) at least 4 mm but less than 6 mm;

x : maximum peel width (both sides) at least 6 mm.

#### For the EG and GA:

+ + : maximum peel width (one side) less than 3 mm;

+ : maximum peel width (one side) at least 3 mm but less than 5 mm;

x : maximum peel width (one side) at least 5 mm.

The test conditions and evaluation scale for salt spray testing were as follows: A cross cut was scribed with an acrylic cutter in the sheet after operation (8) as described above, and the specimen thus prepared was tested using a salt spray tester (5 % by weight solution of sodium chloride in water) maintained at 35 °C. After the stipulated time (based on Japanese Industrial Standard Z-2371), the specimen was rinsed with water and the status of corrosion at the cross cut was evaluated using the following three-level scale:

For the CRS (salt spray test time = 960 hours):

+ + : maximum rust width (both sides) less than 4 mm;

+ : maximum rust width (both sides) at least 4 mm but less than 5 mm;

x : maximum rust width (both sides) at least 5 mm.

For the EG and GA (salt spray test time = 480 hours):

+ + : maximum rust width (one side) less than 4 mm;

maximum rust width (one side) at least 4 mm but less than 5 mm;

maximum rust width (one side) at least 5 mm.

Details of the surface conditioning processes and phosphate treatment processes for the Examples and Comparative Examples and the corresponding test results are reported in the following tables, in which the following abbreviations are used:

## for the phosphate salt component:

Zn2FeP2

= Zn₂Fe(PO₄)₂•4H₂O

Zn3P2

Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>•4H<sub>2</sub>O

Zn2CaP2 =

Zn<sub>2</sub>Ca(PO<sub>4</sub>)<sub>2</sub>•4H<sub>2</sub>O

# for the surfactant component:

EO11NPE

polyoxyethylene (EO: 11) nonylphenol ether

# for the phosphorus compounds:

**ATMPA** 

aminotrimethylenephosphonic acid

1-HEDPA =

1-hydroxyethylidene-1,1-diphosphonic acid

2-HEDPA =

2-hydroxyethylidene-1,1-diphosphonic acid

EDATMPA =

ethylenediaminetetramethylenephosphonic acid.

## other:

Deg.

= Degree

Polym. =

Polymerization

Ex.

Example

=

Comp. Ex.

Comparative Example

VA

vinyl acetate

**PVAIC** 

polyvinylalcohol

Wt%

Percent by weight.

Table 1: EXAMPLES 1 TO 5

				Exan	iple Numbe	r:	
			1	2	3	4	5
	PREP	ALENE®-ZN, g/l	none	none	none	none	none
Ī		Abbreviation	Zn2FeP2	Zn2FeP2	Zn2FeP2	Zn2FeP2	Zn2FeP2
	Phosphate Particles:	Particle size, µm	0.5	0.5	0.5	0.5	0.5
Surface	i ai ticles.	Concentration, g/l	1	1	1	1	1
Ī		Monosaccharide Unit	glucose	glucose	glucose	glucose	fructose
Surface	Sacchar-	Substituent(s)	CH <sub>2</sub> COO	CH <sub>2</sub> COO	CH <sub>2</sub> COO	none	none
	ide-Based Constitu-		NO <sub>2</sub>	NO <sub>2</sub>	H		
9	ents:	Deg. of Substitution	≤ 1.8	≤ 1.8	0.7	none	0
ment		Deg. of Polym.	≤ 3,000	≤ 3,000	≤ 100	1	≤ 100
Com-		Concentration, ppm	5	1,000	10	2,000	2,000
posi- tion	Salt con- stituent(s)	Chemical Formula	none	none	NaNO <sub>2</sub>	MgSO <sub>4</sub> • 7H <sub>2</sub> O	none
Con-	:	Concentration, g/l	none	none	0.5	0.5	none
stitu- ents	ı			11			

Process Conditions:

[	Sur-	Abbreviation	none	none	none	none	none
	factant Constit- uents:	Concentration, g/l	none	none	none	none	none
Ī	Treatmen	it Temperature, °C	20	20		20	
	Treatm	ent Time, Seconds	30	30	30	30	30
		PO <sub>4</sub> 3-	10	15	20	18	16
		Zn <sup>2+</sup>	0.8	1.3	2.2	1.5	1.4
		Mg <sup>2+</sup>	2.0	none	none	none	2.5
Phos-		Co <sup>2+</sup>	none	1.0	none	none	none
phate		Mn <sup>2+</sup>	0.5	none	1.0	none	none
Con-	~	Ca <sup>2+</sup>	none	none	none	1.5	none
version Treat-	Grams per Liter	Sr <sup>2+</sup>	none	none	none	none	0.9
ment	of:	WO <sub>4</sub> -2	none	none	0.3	none	none
Com-		NO <sub>3</sub> -	8.3	7.6	9.0	8.0	7.3
posi- tion		F-	0.1	none	0.1	none         none           20         20         20           30         30         30           20         18         16           2.2         1.5         1.4           none         none         2.5           none         none         none           none         none         none           none         0.9         0.3           none         none         none           9.0         8.0         7.3	0.1
Con-		NO <sub>2</sub> -	0.01	none	0.01	none	0.01
stitu-		NH <sub>4</sub> OH	none	1.5	none	3.0	none
ents and	Treatme	nt Temperature, °C	40	45	50	35	43
Process Condi- tions:		ent Time, Seconds	120	120	120	120	120

Table 2: EXAMPLES 6 TO 10

				Ex	ample Num	ber:	
			6	7	8	9	10
	PREPA	ALENE®-ZN, g/l	none	none	none	none	none
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn2CaP2
	Phosphate	Particle size, µm	0.5	0.6	1.2	0.4	0.4
	Particles:	Concentration, g/l	1	1	1	10	5
		Monosaccharide Unit	glucose	glucose	glucose	glucose	fructose
			xylose				
CC			galactose				
Surface Condi-		Substituent(s)	none	CH <sub>2</sub> COOH		CH <sub>2</sub> COOH	none
tioning	PREPALENE®-ZN, g/l   none   none				1.0		
Treat-	ents:						0
ment					≤ 1,000	≤ 2,000	≤ 500
Com-					1	10	5
1.		Chemical Formula	none	none		Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> • 12H <sub>2</sub> O
Com- position Constit- uents and	stituent(s).	Concentration, g/l	none	none	5	1	10
	Surfactant	Abbreviation	none	none	none	none	EO11NPE
	l	Concentration, g/l	none	none	none	none	2.0
	Treatmen	t Temperature, °C	20	20	20	20	40
1.02.00	Treatme	ent Time, Seconds	30	30	30	30	120
			11	15	22	18	16
		Zn <sup>2+</sup>	0.9	1.3	2.0	1.5	1.4
		Mg <sup>2+</sup>	2.0	none	none	none	2.5
Phos-		Co <sup>2+</sup>	none	none	none	none	none
phate		Mn <sup>2+</sup>	0.6	none	1.0	none	none
Conver-			none	none	none	1.0	none
sion Treat-	Cromo		none	none	none	none	0.9
ment		$WO_4$ -2	none	none	0.3	none	none
Compo-		NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3
sition	<b>V1.</b>		0.1	none	0.1	none	0.1
Constit-			0.01	none	0.01	none	none
uents						3.0	3.5
and	Treatmen	it Temperature, °C	38	43	49	55	59
Process	Treatme	ent Time, Seconds	120	120	120	120	120
Conditions:							

Table 3: COMPARATIVE EXAMPLES 1 TO 5

				Comparativ	e Example l	Number:		
			1	2	3	4	5	
	PREP.	ALENE®-ZN, g/l	none	none	none	none	none	
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn3P2	Zn3P2	
	Phosphate	Particle size, µm	0.5	0.6	1.2	0.5	0.5	
	Particles:	Concentration, g/l	1	1	1	1	1	
	Saashar	Monosaccharide Unit	glucose xylose galactose	glucose	glucose	glucose	fructose	
Surface Condi-	Sacchar- ide-Based Constitu-	Substituent(s)	none		ČH3	none	none	
tioning Treat-	ents:	Deg. of Substitution	0		1.9	none	none	
ment	•	Deg. of Polym.	none	≤ 100				
Com-		Concentration, ppm	100	100	11		2000	
position Constit-	Salt con- stituent(s):	Chemical Formula	none	none	Na <sub>2</sub> O • SiO 2 • 5H <sub>2</sub> O	none         none         n           Zn3P2         Zn3P2         Zn           1.2         0.5         0           1         1         1           glucose         fru           CH2COOH         none         n           CH3         none         n           1.9         none         n           ≤ 1,000         1         ≤           1         2000         2           Ia2O SiO         MgSO4         n           2 *5H2O         *7H2O         n           5         0.5         n           none         none         n           none         none         n           1.0         18         2           2.0         1.5         n           none         none         n           none         none         n           none         none         n           0.3         none         n           0.1         none         n           0.01         none         n           0.01         none         n           0.01         none         n		
uents		Concentration, g/l	none	none	5	0.5	none	
and	Surfactant	Abbreviation	none	none	none	none	none	
Process Condi-	Constit- uents:	Concentration, g/l	none	none	none none		none	
tions:	Treatmen	nt Temperature, °C	20	20	20	20	20	
	Treatm	ent Time, Seconds	30	30	30	30	30	
		PO <sub>4</sub> 3-	11	15	1.0	18	16	
		Zn <sup>2+</sup>	0.1	7.0	2.0	1.5	1.4	
Phos-		Mg <sup>2+</sup> Co <sup>2+</sup>	2.0	none	none	none	2.5	
phate		Co <sup>2+</sup>	none	none	none	none	none	
Conver-		Mn <sup>2+</sup>	0.6	none	1.0	1.0	none	
sion		Ca <sup>2+</sup>	none	none	none	none	none	
Treat-		Sr <sup>2+</sup>	none	none	none	3.0	0.9	
Compo		$WO_4^{-2}$	none	none	0.3	none	none	
Compo- sition	Grams	NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3	
Constit-	1 1 177-		0.1	none	0.1	none	0.1	
uents	of:	NO <sub>2</sub> -	0.01	none	0.01	none	none	
and		NH <sub>4</sub> OH	none	1.5	none	3.0	3.5	
Process	Treatmer	nt Temperature, °C	38	43	49	55	20	
Condi- tions:	Treatme	ent Time, Seconds	120	120	120	120	120	

Table 4: COMPARATIVE EXAMPLES 6 TO 10

				Compa	rative Exan	ple Number	:
			6	7	8	9	10
	PREP	ALENE®-ZN, g/l	1	none	none	none	none
		Abbreviation	none	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, µm	none	0.6	6.5	0.4	0.5
	Particles:	Concentration, g/l	none	1	1	10	0.00001
	·	Monosaccharide Unit	none	none	glucose	glucose	glucose
	Sacchar-	Substituent(s)	none	none	СН <sub>2</sub> СООН СН <sub>3</sub>	CH <sub>2</sub> COOH	CH <sub>2</sub> COOH
Surface	ide-Based Constitu-	Deg. of Substitution	none	none	1.9	1.0	0.7
Condi-	ents:	Deg. of Polym.	none	none	≤ 1,000	≤ 2,000	≤ 100
tioning Treat-	02331	Concentration, ppm	none	none	1	5,000	10
ment Com- s	Salt con- stituent(s):	Chemical Formula	none	none	Na <sub>2</sub> O•SiO <sub>2</sub> •5H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	NaNO <sub>2</sub>
	` ,	Concentration, g/l	none	none	5	1	0.5
	Surfactant	Abbreviation	none	none	none	none	none
uents and	Constit- uents:	Concentration, g/l	none	none	none	none	none
Process		nt Temperature, °C	20	20	20	20	20
Condi- tions:	Treatm	ent Time, Seconds	30	30	30	30	30
		PO <sub>4</sub> 3-	11	15	22	18	16
		Zn <sup>2+</sup>	0.9	1.3	2.0	1.5	1.4
		Mg <sup>2+</sup>	2.0	none	none	none	2.5
Phos-		Co <sup>2+</sup>	none	none	none	none	none
phate		Mn <sup>2+</sup>	0.6	none	1.0	none	none
Conver-		Ca <sup>2+</sup>	none	none	none	1.0	none
sion Treat-		Sr <sup>2+</sup>	none	none	none	none	0.9
ment		$WO_4^{-2}$	none	none	0.3	none	none
Compo-		NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3
sition	Grams	F-	0.1	none	0.1	none	0.1
Constit-		NO <sub>2</sub> -	0.01	none	0.01	none	none
uents	of:	NH <sub>4</sub> OH	none	1.5	none	3.0	3.5
and	Treatme	nt Temperature, °C	40	45	50	39	43
Process Condi- tions:		ent Time, Seconds	120	120	120	120	120

Table 5: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR EXAMPLES 1 THROUGH 10

TEST OR OTHER RATING	SUB-		•	E	XAMP.	LE N	UMBI	ER			
	STRATE TESTE D	1	2	3	4	5	6	7	8	9	10
Coating Appearance	CRS	+	+	+	+	+	+	+	+	+	+
	EG	+	+	+	+	+	+	+	+	+	+
	GA	+	+	+	+	+	+	+	+	+	+
Secondary (Water-Resistant)	CRS	+	++	++	++	++	++	++	++	++	++
Adherence	EG	+	++	+	++	++	++	++	+	++	++
	GA	++	++	+	++	++	++	++	+	++	++
	CRS	++	++	++	++	+	++	+	++	++	+
Resistance to Hot Salt Water	EG	++	++	++	++	++	++	+	++	++	++
	GA	++	++	++	++	++	++	+	++	++	++
	CRS	+	++	++	+	+	+	+	+	++	+
Resistance to Salt Spray	EG	++	+	++	+	++	++	+	+	++	++
	GA	++	+	++	+	++	++	+	+	++	++

Table 6: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR COMPARISON EXAMPLES 1 THROUGH 10

TEST OR OTHER RATING	SUB-		C	OMPAR	ISON ]	EXAN	1PLE	Num	BER		
	STRATE TESTE D	1	2	3	4	5	6	7	8	9	10
	CRS	×	+	×	×	×	+	×	×	×	×
Coating Appearance	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	++	+	++	++	++	+	++	++	+	+
Secondary (Water-Resistant)	EG	×	×	×	×	×	×	×	×	×	×
Adherence	GA	×	×	×	×	×	×	×	×	×	×
	CRS	×	++	×	×	×	++	×	×	×	×
Resistance to Hot Salt Water	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	×	×	×	×	×	×	×	×	×	×
Resistance to Salt Spray	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

Table 7: EXAMPLES 11 TO 15

				Exa	ample Num	ber:	
			11	12	13	14	15
	PREPA	ALENE®-ZN, g/l	none	none	none	none	none
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, µm	0.5	0.5	1.7	0.6	0.5
	Particles:	Concentration, g/l	5	1	1	5	10
	Phosphor-	Substance	tripoly-	hexameta-	ATMPA	1-HEDPA	EDATMPA
	us Con-		phos-	phosphoric			
Sfooo	taining		phoric	acid			
_	Solute:		acid_				
B 1		Concentration, ppm	1	100	500	50	1,000
	Salt con-	Chemical Formula		Na <sub>2</sub> O•SiO	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> •1
	stituent(s):		7H <sub>2</sub> O	2•5H2O		<u> </u>	2H <sub>2</sub> O
		Concentration, g/l	0.5	1	none	5	10
	Surfactant	Abbreviation	none	none	none	none	EO11NPE
Surface Conditioning Treatment Composition Constituents and Process Conditions:  Phosphate Conversion Treatment Composition Constituents	Constit-	Concentration, g/l	none	none	none	none	2.0
uents	uents: Treatment Temperature, °C		20	20	20	20	40
and			20 30	20	20 30	20	40
			30	30	30	30	120
	·						
tions:							
		PO <sub>4</sub> 3-	10	15	20	18	16
		Zn <sup>2+</sup>	0.8	1.3	2.2	1.5	1.4
Dhaa		Mg <sup>2+</sup>	2.0	none	none	none	2.5
		Co <sup>2+</sup>	none	1.0	none	none	none
1 -		Mn <sup>2+</sup>	0.5	none	1.0	none	none
		Ca <sup>2+</sup>	none	none	none	1.5	none
		Sr <sup>2+</sup>	none	none	none	none	0.9
		WO <sub>4</sub> -2	none	none	0.3	none	none
		NO <sub>3</sub> -	8.3	7.6	9.0	8.0	7.3
_	Grams	F-	0.1	none	0.1	none	0.1
Constit-	per Liter	NO <sub>2</sub> -	0.01	none	0.01	none	0.01
uents	of:	NH <sub>4</sub> OH	none	1.5	none	3.0	none
		t Temperature, °C	40	45	50	39	43
	Treatme	ent Time, Seconds	120	120	120	120	120
1							
tions:			ļ	<u> </u>			

Table 8: COMPARATIVE EXAMPLES 11 TO 15

	<u> </u>			Comparativ	e Example	Number:	
			11	12	13	14	15
	PREPA	LENE®-ZN, g/l	none	none	none	none	none
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, µm	0.5	0.5	1.7	0.6	0.5
	Particles:	Concentration, g/l	5	1	1	5	10
,	Phosphor-	Substance	tripoly-	hexameta-	ATMPA	2-	EDATMPA
	us Con-		phos-	phosphoric		HEDPA	
Surface	taining		phoric	acid			
Condi-	Solute:		acid				1.000
tioning		Concentration,	1	100	500	50	1,000
Treat-		ppm Chemical Formula	Masou	NaOH		No. CO.	No - PO 1
ment Com-	Salt con-	Cnemical Formula	MgSO <sub>4</sub> ●7H <sub>2</sub> O	NaOn	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> •1 2H <sub>2</sub> O
position	stituent(s):	Concentration, g/l	0.5	1	none	5	10
Constit-	Surfactant		none	none	none	none	EO11NPE
uents	Constit-	Concentration, g/l	none	none	none	none	2.0
and	uents:	Concentration, g/i	none	l none	lione	none	2.0
Process Condi-	Treatmen	t Temperature, °C	20	20	20	20	40
tions:	Treatme	nt Time, Seconds	30	30	30	30	120
		PO <sub>4</sub> 3-	11	15	1.0	18	16
		Zn <sup>2+</sup>	0.1	7.0	2.0	1.5	1.4
Diver		Mg <sup>2+</sup>	2.0	none	none	none	2.5
Phos- phate		Co <sup>2+</sup>	none	none	none	none	none
Conver-		Mn <sup>2+</sup>	0.6	none	1.0	1.0	none
sion		Ca <sup>2+</sup>	none	none	none	none	none
Treat-		Sr <sup>2+</sup>	none	none	none	3.0	0.9
ment		WO <sub>4</sub> -2	none	none	0.3	none	none
Compo- sition	Grams	NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3
Constit-		F-	0.1	none	0.1	none	0.1
uents	of:	NO <sub>2</sub> -	0.01	none	0.01	none	none
and		NH <sub>4</sub> OH	none	1.5	none	3.0	3.5
Process	Treatmen	t Temperature, °C	40	45	50	39	20
Condi- tions:	Treatme	ent Time, Seconds	120	120	120	120	120

Table 9: COMPARATIVE EXAMPLES 16 TO 20

				Compa	arative E	xample Numbe	r:
			16	17	18	19	20
	PREP	ALENE®-ZN, g/l	1	none	none	none	none
		Abbreviation	none	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, μm	none	0.5	6.5	0.6	0.00001
	Particles	Concentration, g/l	none	1	1	5	10
]	Phosphor-	Substance	none	none	ATMPA	hexametaphos-	EDATMPA
	us Ĉon-				i	phoric acid	
Surface	taining Solute	Concentration, ppm	none	none	500	3,000	1,000
Condi-	Salt con- stituent(s)	Chemical Formula	MgSO <sub>4</sub>	none	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> O•SiO <sub>2</sub> •5H <sub>2</sub> O
Treat-	Situent(s)		7H <sub>2</sub> O				
ment		Concentration, g/l	0.5	none	none	5	1
Com- position	Surfactant	Abbreviation	none	none	none	none	EO11NPE
Constit-	Constit- uents	Concentration, g/l	none	none	none	none	2.0
uents and	Treatme	nt Temperature, °C	20	20	20	20	40
Process	Treatm	ent Time, Seconds	30	30	30	30	120
Condi- tions:					ii		
		PO <sub>4</sub> 3-	11	15	22	18	16
	ľ	Zn <sup>2+</sup>	0.9	1.3	2.0	1.5	1.4
Phos-		Mg <sup>2+</sup> Co <sup>2+</sup>	2.0	none	none	none	2.5
phate		Co <sup>2+</sup>	none	none	none	none	none
Conver-		Mn <sup>2+</sup>	0.6	none	1.0	none	none
sion		Ca <sup>2+</sup>	none	none	none	1.0	none
Treat-		Sr <sup>2+</sup>	none	none	none	none	0.9
ment	Grams	WO <sub>4</sub> -2	none	none	0.3	none	none
Compo- sition	per Liter of:	NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3
Constit-		F-	0.1	none	0.1	none	0.1
uents		NO <sub>2</sub> -	0.01	none	0.01	none	none
and		NH <sub>4</sub> OH	none	1.5	none	3.0	3.5
Process	Treatme	nt Temperature, °C	40	45	50_	39	43
Condi- tions:	Treatm	ent Time, Seconds	120	120	120	120	120

Table 10: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR EXAMPLES 11 THROUGH 15

TEST OR OTHER RATING	SUBSTRATE		EXAM	IPLE NUM	IBER	
	TESTED	11	12	13	14	15
Coating Appearance	CRS	+	+	+	+	+
	EG	+	+	+	+	+
	GA	+	+	+	+	+
	CRS	++	++	++	++	++_
Secondary (Water-Resistant)	EG	++	++	+	++	++
Adherence	GA	++	++	+	++	++
	CRS	++	++	++	++	+
Resistance to Hot Salt Water	EG	++	++	+ +	++	++
	GA	++	++	++	++	++
	CRS	+	++	++	+	+
Resistance to Salt Spray	EG	++	+	++	+	++
	GA	++	+	++	+	++

Table 11: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR COMPARISON EXAMPLES 11 THROUGH 20

TEST OR OTHER RATING	SUB-		Co	OMPAR	ISON ]	EXAN	1PLE	Num	BER		
	STRATE TESTE D	11	12	13	14	15	16	17	18	19	20
	CRS	×	+	×	×	×	+	×	×	×	×
Coating Appearance	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	++	+	++	++	++	+	++	++	++	+
Secondary (Water-Resistant)	EG	×	×	×	×	×	×	×	×	×	×
Adherence	GA	×	×	×	×	×	×	×	×	×	×
	CRS	×	++	×	×	×	++	×	×	×	×
Resistance to Hot Salt Water	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	×	×	×	×	×	×	×	×	×	×
Resistance to Salt Spray	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

Table 12: EXAMPLES 16 TO 20

				Exa	ample Num	ber:	
_			16	17	18	19	20
	PREPA	LENE®-ZN, g/l	none	none	none	none	none
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, µm	0.5	1.5	0.5	1.6	0.3
	Particles	Concentration, g/l	5	8	1	5	10
	Water	Substance Name	polyvinyl	carboxyl-	sulfonic	Copolymer	
	Soluble		alcohol	modified	acid-	with VA	r with VA
	VA	i		PVAlc	modified		
Surface	Polymer				PVAlc		
Condi-	or	Comonomer with	none	none	none	maleic acid	crotonic
tioning Treat-	Derivative	VA					acid
ment		Comonomer % by	none	none	none	80	70
Com-		Weight					
position		Concentration, ppm	1	500	2,000	1,000	10
Constit-	Salt con-	Chemical Formula		Na <sub>2</sub> O•SiO	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>
uents	stituent(s)		•7H <sub>2</sub> O	2			•12H <sub>2</sub> O
and			0.5	•5H <sub>2</sub> O			1.0
Process		Concentration, g/l	0.5	1	none	5	10
Condi-	Surfactant		none	none	none	none	EO11NPE
tions:	Constit-	Concentration, g/l	none	none	none	none	2.0
	uents	4 TC 9 C	20	20	20	20	40
		t Temperature, °C	30	30	30	30	120
	1 reatmo	ent Time, Seconds		15		18	16
		PO <sub>4</sub> 3- Zn <sup>2+</sup>	10	1.3	20	1.5	
		Mg <sup>2+</sup>	0.8 2.0		2.2		1.4 2.5
Phos-		Co <sup>2+</sup>		none	none	none	
phate		Mn <sup>2+</sup>	none	1.0	none	none	none
Conver-		Ca <sup>2+</sup>	0.5	none	1.0	none 1.5	none
sion		Sr <sup>2+</sup>	none	none	none		none
Treat-	Grams		none	none	none	none	0.9
ment	per Liter	WO <sub>4</sub> -2	none	none	0.3	none	none
Compo-	of:	NO <sub>3</sub> -	8.3	7.6	9.0	8.0	7.3
sition		F-	0.1	none	0.1	none	0.1
Constit-		NO <sub>2</sub> -	0.01	none	0.01	none	0.01
uents		NH <sub>4</sub> OH	none	1.5	none	3.0	none
and		t Temperature, °C	40	45	50	39	43
Process	Treatmo	ent Time, Seconds	120	120	120	120	120
Condi-				1			
tions:			<u> </u>	<u></u>			

Table 13: COMPARATIVE EXAMPLES 21 TO 25

<u> </u>			-	Comparative	Example N	Number:	
			21	22	23	24	25
	PREPA	LENE®-ZN, g/l	none	none	none	none	none
		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn3P2
	Phosphate	Particle size, µm	0.5	0.5	0.5	1.6	0.5
1	Particles:	Concentration, g/l	5	1	1	5	1
	Water Soluble	Substance Name	polyvinyl- alcohol	carboxyl- modified	sulfonic acid-modi-	Copoly- mer with	Copoly- mer with
Surface	VA			PVAlc	fied PVAlc	VA	VA
Condi- tioning	Polymer or	Comonomer with VA	none	none	none	maleic acid	crotonic acid
Treat- ment	:	Comonomer % by Weight	none	none	none	80	70
Com- position		Concentration, ppm	1	500 2,000		1,000	10
Constit-	Salt con- stituent(s):	Chemical Formula	MgSO <sub>4</sub> • 7H <sub>2</sub> O	Na <sub>2</sub> O•SiO <sub>2</sub> •5H <sub>2</sub> O	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> •12H <sub>2</sub> O
uents and	stitueni(s).	Concentration, g/l	0.5	1	none	5	10
Process	Surfactant	Abbreviation	none	none	none	none	EO11NPE
Condi-	Constit- uents:	Concentration, g/l	none	none	none	none	2.0
tions:		Temperature, °C	20	20	20	20	40
	Treatment Time, Seconds		30	30	30	30	120
		PO <sub>4</sub> 3-	11	15	1.0	18	16
ļ		Zn <sup>2+</sup>	0.1	7.0	2.0	1.5	1.4
Phos-		Mg <sup>2+</sup>	2.0	none	none	none	2.5
phate		Co <sup>2+</sup>	none	none	none	none	none
Conver-	,	Mn <sup>2+</sup>	0.6	none	1.0	1.0	none
sion	į .	Ca <sup>2+</sup>	none	none	none	none	none
Treat-	Grams per Liter	Sr <sup>2+</sup>	none	none	none	3.0	0.9
ment	of:	WO <sub>4</sub> -2	none	none	0.3	none	none
Compo-		NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3
sition		F-	0.1	none	0.1	none	0.1
Constit-		NO <sub>2</sub> -	0.01	none	0.01	none	none
uents	•	NH <sub>4</sub> OH	none	1.5	none	3.0	3.5
and		t Temperature, °C	40	45	50	39	20
Process Condi-	Treatme	nt Time, Seconds	120	120	120	120	120
tions:	<u></u>			<u> </u>	<u> </u>	<u> </u>	

Table 14: COMPARATIVE EXAMPLES 26 TO 30

	1			Comparativ	e Example	Number:	
			26	27	28	29	30
	PREP.	ALENE®-ZN, g/l	1	none	none	none	none
		Abbreviation	none	Zn2FeP2	Zn3P2	Zn2CaP2	Zn2FeP2
	Phosphate	Particle size, µm	none	1.7	6.5	1.6	0.3
	Particles:	Concentration, g/l	none	7	1	5	0.00001
	Water	Substance Name	polyvinyl		sulfonic	Copoly-	Copoly-
	Soluble		alcohol	none	acid-	mer with	mer with
C	VA				modified	VA	VA
Surface Condi-	Polymer				PVAlc		
	or	Comonomer with VA	none	none	none	maleic	crotonic
Treat-	<b>Derivative</b>					acid	acid
ment	:	Comonomer % by	none	none	none	80	70
Com-		Weight	•		2 000	2.000	10
position	× ====	Concentration, ppm	1	none	2,000	3,000	10
Constit-	Salt con-	Chemical Formula	none	Na <sub>2</sub> O•SiO	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>
uents	stituent(s):			•5H <sub>2</sub> O			•12H <sub>2</sub> O
and		Consentuation of		1		5	10
Process	Surfactant	Concentration, g/l Abbreviation	none	nono	none		EO11NPE
Condi-	Constit-	Concentration, g/l	none	none	none	none	2.0
tions:	uents:	Concentration, g/i	none	none	none	none	2.0
		nt Temperature, °C	20	20	20	20	40
	Treatment Time, Seconds		30	30	30	30	120
<b></b>	Hicatin	PO <sub>4</sub> 3-	10	15	20	18	16
		Zn <sup>2+</sup>	0.8	1.3	2.2	1.5	1.4
		M <sub>G</sub> 2+	2.0	none	none	none	2.5
Phos-		Mg <sup>2+</sup> Co <sup>2+</sup>	none	1.0	none	none	none
phate		Mn <sup>2+</sup>	0.5	none	1.0	none	none
Conver-		Ca <sup>2+</sup>	none	none	none	1.5	none
sion		Sr <sup>2+</sup>	none	none	none	none	0.9
Treat-	Grams	WO <sub>4</sub> -2	none	none	0.3	none	none
ment	per Liter	NO <sub>3</sub> -	8.3	7.6	9.0	8.0	7.3
Compo-	of:	F-	0.1	none	0.1	none	0.1
sition Constit-		NO <sub>2</sub> -	0.01	none	0.01	none	0.01
uents		NH <sub>4</sub> OH	none	1.5	none	3.0	none
and	Treatme	nt Temperature, °C	40	45	50	39	43
Process		ent Time, Seconds	120	120	120	120	120
Condi-							
tions:							
	·			1	L		L

Table 15: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR EXAMPLES 16 THROUGH 20

TEST OR OTHER RATING	SUBSTRATE	EXAMPLE NUMBER							
	TESTED	16	17	18	19	20			
Coating Appearance	CRS	+	+	+	+	+			
	EG	+	+	+	+	+			
	GA	+	+	+	+	+			
Secondary (Water-Resistant)	CRS	++	++	++	++	++			
Adherence	EG	++	++	+	++	++			
	GA	++	++	+	++	++			
	CRS	++	++	++	++	+			
CRS	++	++	++	++	++				
	GA	++	++	++	++	++			
	CRS	+	++	++	+	+			
Resistance to Salt Spray	EG	++	+	++	+	++			
	GA	++	+	++	+	++			

Table 16: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR COMPARISON EXAMPLES 21 THROUGH 30

TEST OR OTHER RATING	SUB-		C	OMPAR	ISON ]	EXAN	1PLE	Num	BER		
	STRATE TESTE D	21	22	23	24	25	26	27	28	29	30
	CRS	×	+	×	×	×	+	×	×	×	×
Coating Appearance	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	+	+	++	++	++	+	++	++	++	+
Secondary (Water-Resistant)	EG	×	×	×	×	×	×	×	×	×	×
Adherence	GA	×	×	×	×	×	×	×	×	×	×
	CRS	×	++	×	×	×	+	×	×	×	×
Resistance to Hot Salt Water	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	×	×	×	×	×	×	×	×	×	×
Resistance to Salt Spray	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×

Table 17: EXAMPLES 21 TO 25 with Type (4) Polymer Adhesion Promoting Agents

	Example Number:												
1			21	22	23	24	25						
	PREPA	LENE®-ZN, g/l	none	none	none	none	none						
i l		Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	Zn2FeP2						
	Phosphate	Particle size, µm	0.5	0.5	1.7	0.6	0.5						
	Particles	Concentration, g/l	5	1	1	5	10						
	Monomer	R <sup>1</sup>	Н	none	none	CH <sub>3</sub>	none						
	with	R <sup>2</sup>	C <sub>2</sub> H <sub>4</sub> OH	none	none	C <sub>3</sub> H <sub>7</sub> OH	none						
	Formula	Wt% in Polymer	100	none	none	20	none						
Surface	(I)												
Condi-	Other Un-	Monomer Name	none	maleic	acrylic	maleic acid	methacrylic						
tioning	saturated Acid	XX/40/ : Dal		acid 80	acid 100	80	acid 50						
Treat-	Monomer	Wt% in Polymer	none	80	100	•0	30						
ment	Other Co-	Monomer Name	none	vinyl	none	none	styrene-						
Com-	monomer	Miduomer Mame	none	acetate	110110		sulfonic acid						
position		Wt% in Polymer	none	20	none	none	50						
Constit-	Polymer C	oncentration, ppm	1	500	2,000	1,500	5						
uents	Salt con-	Chemical	MgSO <sub>4</sub>	Na <sub>2</sub> O•Si	none	KOH	Na <sub>3</sub> PO <sub>4</sub> •12H <sub>2</sub> O						
and	stituent(s)	Formula	•7H2O	O <sub>2</sub> •5H <sub>2</sub> O			•12H2O						
Process	Stituent(s)		_	•5H <sub>2</sub> O									
Condi-		Concentration, g/l	0.5	1	none	5	10						
tions:	Surfactant		none	none	none	none	EO11NPE						
	Constit-	Concentration, g/l	none	none	none	none	2.0						
	uents	Townson	20	-20	20	20	40						
	Treatment	Temperature, °C nt Time, Seconds	30	20 30	30	30	120						
	1 reatine	DO 3-	10	15	20	18	16						
		PO <sub>4</sub> 3- Zn <sup>2+</sup>	0.8	1.3	2.2	1.5	1.4						
		Mg2+	2.0	none	none	none	2.5						
Phos-		Co <sup>2+</sup>	none	1.0	none	none	none						
phate		Mn <sup>2+</sup>	0.5	none	1.0	none	none						
Conver-		Ca <sup>2+</sup>	none	none	none	1.5	none						
sion		Sr <sup>2+</sup>	none	none	none	none	0.9						
Treat-	Grams per Liter	WO <sub>4</sub> -2	none	none	0.3	none	none						
ment	per Liter of:	NO <sub>3</sub> -	8.3	7.6	9.0	8.0	7.3						
Compo-		F-	0.1	none	0.1	none	0.1						
sition		NO <sub>2</sub> -	0.01	none	0.01	none	0.01						
Constit-		NH <sub>4</sub> OH	none	1.5	none	3.0	none						
	Treatment	t Temperature, °C	40	45	50	39	43						
uents	Treatme	nt Time, Seconds	120	120	120	120	120						
and													
Process				1	1								
Condi-													
tions:			l	<u> </u>	<u> </u>	<u> </u>							

Table 18: COMPARATIVE EXAMPLES 31 TO 35

Comparative Example Number:												
		1	<del></del>		Tative Exam	34	35					
			31	32			none					
L	PREPAI	LENE®-ZN, g/l	none	none	none	none	Zn2FeP2					
	DI 1 4 .	Abbreviation	Zn2FeP2	Zn3P2	Zn3P2	Zn2CaP2	0.5					
	Phosphate	Particle size, µm	0.5	0.5	1.7	0.6	10					
	Particles	Concentration,	5	1	1	5	10					
		R!			mana	CHA	none					
	Monomer	R:	H	none	none	CH3 C3H7OH	none					
Surface	with Formula	$\mathbb{R}^2$	$C_2H_4OH$	none	none	20	none					
		Wt% in Polymer	100	none	none	20	Hone					
Condi-	Other Un-	Monomer Name	none	maleic	acrylic acid	maleic acid	methacrylic					
tioning	saturated	With the state of	none	acid		11141114 4614	acid					
Treat-	Acid	Wt% in Polymer	none	80	100	80	50					
	Monomer	vve /o in r ory mer	110110	00	1							
ment	Other Co-	Monomer Name	none	vinyl	none	none	styrenesul-					
Com-	monomer			acetate			főnic acid					
position		Wt% in Polymer	none	20	none	none	50					
Constit-	Polymer Co	oncentration, ppm	I	500	2,000	1,500	5					
Constit-		Chemical	MgSO <sub>4</sub> •7H <sub>2</sub> O	Na2O•Si	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> • 12H <sub>2</sub> O					
uents	Salt con-	Formula	•7H2O	U2			•12H <sub>2</sub> O					
and	stituent(s)		_	•5H <sub>2</sub> O								
Process		Concentration,	0.5	i	none	5	10					
		g/l										
Condi-	Surfactant		none	none	none	none	EOTINPE					
tions:	Constit-	Concentration,	none	none	none	none	2.0					
	uents	g/l			- 70		40					
	Treatment	Temperature, °C	20	20	20	20	40					
	Treatmer	it Time, Seconds	30	30	30	30	120					
		PO <sub>4</sub> 3-	11	15	1.0	18	16					
		Zn2T	0.1	7.0	2.0	1.5	1.4					
l		Mg2+	2.0	none	none	none	2.5					
Phos-	1	Co2+ Mn2+	none	none	none	none	none					
phate		Mn2	0.6	none	1.0	1.0	none					
Conver-		Ca2+ Sr2+	none	none	none	none	none					
		Sr <sup>2</sup>	none	none	none	3.0	0.9					
sion		WO <sub>4</sub> -2	none	none	0.3	none	none					
Treat-		NO <sub>3</sub> -	8.9	7.6	9.0	8.0	7.3					
ment	Grams	F-	0.1	none	0.1	none	0.1					
	per Liter	NO <sub>2</sub> -	0.01	none	0.01	none	none					
Compo-	of:	NH4OH	none	1.5	none	3.0	3.5					
sition		Temperature, °C	40	45	50		20					
Constit-	Treatmer	nt Time, Seconds	120	120	120	120	120					
uents	l			1								
	ĺ				1		1					
and	1			1			1					
Process					1	}	1					
Condi-						!						
			Į.		1	1	ĺ					
tions:				<u> </u>	<u> </u>		1					

Table 19: COMPARATIVE EXAMPLES 36 TO 40

<del></del>				Comparativ	e Example	Number:	
			36	37	38	39	40
	PREP	ALENE®-ZN, g/I	1	none	none	none	none
1		Abbreviation	none	Zn2CaP2	Zn3P2	Zn2CaP2	Zn2FeP2
Surface	Phosphate	Particle size, µm	none	0.8	6.8	0.6	0.5
Condi-	Parficles	Concentration, g/l	none	10		5	0.0001
	Monomer	R1	Н	none	none	CH <sub>3</sub>	none
tioning	_ with .	$\mathbb{R}^2$	C <sub>2</sub> H <sub>4</sub> OH	none	none	C3H7OH	none
Treat- ment	Formula (I)	Wt% in Polymer	100	none	none	20	none
Com-	Other Un- saturated	Monomer Name	none	none	acrylic acid	maleic acid	metha- crylic acid
position	Acid Monomer	Wt% in Polymer	none	none	100	80	50
Constit- uents	Other Co- monomer	Monomer Name	none	none	none	none	styrenesul -fonic acid
and		Wt% in Polymer	none	none	none	none	50
	Polymer	Concentration, ppm		none	2,000	3,000	5
Process Condi-	Salt con-	Chemical Formula	MgSO <sub>4</sub> •7H <sub>2</sub> O	Na <sub>2</sub> O•SiO	none	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub> •12H <sub>2</sub> O
tions:	stituent(s)			•5H <sub>2</sub> O			
tions.		Concentration, g/l	0.5	1	none	5	10
	Surfactant	Abbreviation	none	none	none	none	EOTINPE
	Constit- uents	Concentration, g/l	none	none	none	none	2.0
		nt Temperature, °C	20	20	20	20	40 120
	Treatm	ent Time, Seconds	30	30	30	30	
		PO43-	10	15	20	18	16 1.4
l		Zn <sup>2+</sup> Mg <sup>2+</sup>	0.8	1.3		1.5	
Phos-		IVI g 2	2.0	none	none	none	2.5
phate		Co2+ Mn2+	none 0.5	1.0	none 1.0	none	none
Conver-		Ca <sup>2+</sup>	none	none	none	none 1.5	none
sion	Grams	Sr <sup>2+</sup>	none	none	none	none	0.9
	per Liter	$\frac{S1^{-}}{WO_{4}^{-2}}$	none	none	0.3	none	none
Treat-	of:	NO3-	8.3	7.6	9.0	8.0	7.3
ment		<u> </u>	0.1	none	0.1	none	0.1
Compo-		NO <sub>2</sub> -	0.01	none	0.01	none	0.01
sition		NH₄ÓH	none	1.5	none	3.0	none
Constit-							
uents	Treatme	nt Temperature, °C	40	45	50	39	43
and		ent Time, Seconds	120	120	120	120	120
1		-,					
Process	1		1				
Condi-	1						
tions:							

Table 20: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR EXAMPLES 21 THROUGH 25

TEST OR OTHER RATING	SUBSTRATE	EXAMPLE NUMBER							
	TESTED	21	22	23	24	25			
Coating Appearance	CRS	+	+	+	+	+			
<b>3 1 1</b>	EG	+	+	+	+	+			
	GA	+	+	+	+	+			
Secondary (Water-Resistant)	CRS	++	++	++	++	++			
Adherence	EG	++	++	+	++	++			
	GA	++	++	23 24 25 + + + + + + + + + + +	++				
	CRS	++	++	++	++	+			
Resistance to Hot Salt Water	EG	++	++	++	++	++			
	GA	++	++	++	++	++			
	CRS	+	++	++	+	+			
Resistance to Salt Spray	EG	++	+	++	+	++			
	GA	++	1_+	++	+	++			

Table 21: APPEARANCE OF THE CONVERSION COATING AND RESULTS OF PAINTING PERFORMANCE TESTING FOR COMPARISON EXAMPLES 31 THROUGH 40

TEST OR OTHER RATING	SUB-		C	OMPAR	ISON ]	EXAN	1PLE	Num	BER		
	STRATE TESTE D	31	32	33	34	35	36	37	38	39	40
	CRS	×	+	×	×	×	+	×	×	×	×
Coating Appearance	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	X	×	×	+
	CRS	++	+	++	++	++	+	++	++	++	+
Secondary (Water-Resistant)	EG	×	×	×	×	×	×	×	×	×	×
Adherence	GA	×	×	×	×	×	×	×	×	×	×
	CRS	×	++	×	×	×	++	×	×	×	×
Resistance to Hot Salt Water	EG	×	+	×	×	×	+	×	×	×	+
	GA	×	+	×	×	×	+	×	×	×	+
	CRS	×	×	×	×	×	×	×	×	×	×
Resistance to Salt Spray	EG	×	+	×	×	×	+	×	×	×	×
	GA	×	×	×	×	×	×	×	×	×	×